

UNITED STATES PATENT OFFICE

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COMPLEX ESTERS AND POLYMERS
THEREOF

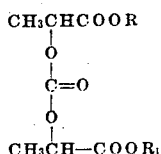
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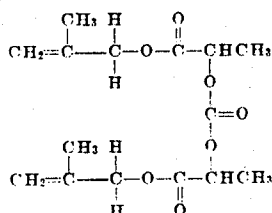
19 Claims. (Cl. 260—78)

This invention relates to novel esters and to the polymers of these esters. In accordance with the present invention, we have discovered a novel class of unsaturated esters of carbonic acid and an ester of lactic acid and an unsaturated alcohol. These esters may be polymerized to form products having high tensile strength and substantially greater resistance to shattering than many of the polymers of other unsaturated esters. The invention is applicable to esters of various unsaturated alcohols but is particularly applicable to allyl, methallyl, vinyl and 2-chloro-allyl esters. Esters of other alcohols such as crotyl, chlorocrotyl, ethyl allyl, cinnamyl, propargyl, methyl vinyl carbonyl, oleyl, ricinoleyl, tiglyl, or isopropenyl vinyl carbonyl alcohol or 3-chlorobutene 2-ol-1, 3-hydroxy butene-1, 3-hydroxy pentadiene-1,4, 1-hydroxy hexadiene-2,4, 1-hydroxy-2-methylhexene-2, or the unsaturated alcohols derived by reduction of coconut oil or China-wood oil acids or other unsaturated or halogenated unsaturated alcohol may also be prepared.

The compounds herein contemplated have the following general formula



where R and R₁ are unsaturated radicals such as hydrocarbon or halohydrocarbon or other unsaturated radical. They may be prepared by reaction of the esters of unsaturated esters of lactic acid with phosgene, preferably in the presence of an alkaline agent such as pyridine, sodium, potassium, barium, strontium, calcium, or magnesium carbonate, bicarbonate, or hydroxide or other alkaline agent. For example, methallyl lactate, when reacted with phosgene forms the diester having the probable formula



Other esters may be formed in similar manner. The esters may be recovered, preferably after removal of pyridine hydrochloride if present, from

the reaction mixture by distillation. However, these materials are high boiling liquids or solids and this is often difficult. Accordingly, the esters are often purified by washing the reaction mixture with water and drying over suitable dehydrating agents such as calcium chloride, active carbon, etc.

The compositions herein described are generally high boiling point liquids but in some cases may be solids. Most of the liquids are very clear and colorless and are miscible with numerous organic solvents such as acetone, alcohol, chloroform, dioxane, benzene, xylene, toluene, ethyl ether, paraffin hydrocarbons, etc.

These compositions may be used for many purposes such as solvents, paint compositions, insecticides, pharmaceuticals, or plasticizers for various materials such as cellulose, vinyl, urea, phenol, acrylic or styrene resins or plastics, etc. In particular, the products are found to polymerize in the presence of catalysts, such as heat, light, oxygen, ozone, peroxides, such as lauryl or benzoyl peroxide, or other oxygen catalyst, etc., to form products of desirable character.

By polymerization of these compounds it is possible to secure a wide range of polymers, some of which are extremely hard, while others are soft, flexible and often rubber-like in character. In general, the polymers thus obtained are transparent and colorless, although the polymer occasionally may be slightly yellow. Many of these materials are found to be superior in strength characteristics to the polymers of allyl or other unsaturated esters of polybasic acids. If desired, the compounds herein described may be cast polymerized to form products having various shapes. These polymers in their finally cured state are substantially infusible and insoluble, and in general, are substantially unaffected by acids, alkalies, water or organic solvents.

In accordance with the present invention, intermediate polymers which are fusible, or thermoplastic also may be prepared. In general, such polymers are soluble in various organic solvents such as acetone, carbon tetrachloride, benzene, xylene, toluene, dioxane, etc. These fusible polymers may be further polymerized to an infusible state to form products similar to the infusible polymers mentioned above. Thus, the fusible polymer may be molded or otherwise shaped and polymerized by means of heat and/or light to form shaped products which are substantially infusible and insoluble which retain their shape permanently.

This method of preparing infusible polymers is

highly advantageous since it is often found that the production of cast polymers is complicated by the formation of fractures, bubbles, or other defects during polymerization. These difficulties are avoided through use of the fusible polymer. In addition, more completely polymerized products are obtainable by this means.

The fusible polymers herein described may be prepared by polymerizing the unsaturated compounds which contain at least two polymerizable unsaturated groups until substantial polymerization has occurred and interrupting polymerization before the polymer is converted into a gel. It is found that when polymerization of these materials is initiated, a fusible polymer is preliminarily formed. As polymerization proceeds, the monomer-polymer mixture is converted into a gel which is substantially infusible. This polymer does not fuse at atmospheric pressure. Further polymerization hardens the polymer to its final state of polymerization. After interrupting the polymerization, it is possible to remove a portion or all of the monomer and to recover the fusible polymer substantially free from monomer or at least as a concentrate containing substantially less monomer than is present in the monomer-polymer mixture formed by ordinary polymerization of undiluted monomer. This interruption of polymerization may be effected by cooling, addition of inhibitors or by other methods as hereinafter more fully described.

In general, it is possible to secure the fusible material in superior yields by polymerizing the monomer in a solution in which the fusible polymer is normally soluble. This polymer is generally soluble in the solvents which are capable of dissolving the usual thermoplastic vinyl or acrylic resins, such as polymethyl methacrylate or acrylonitrile. Thus, such solvents as acetone, dioxane, chloroform, toluene, benzene, carbon tetrachloride, methyl cellosolve acetate, phenyl cellosolve, dichloroethyl ether, xylene, tetralin, dibutyl phthalate, trichloroethylene, tetrachloroethane, etc., or mixtures of these solvents generally are found to be suitable. Solutions having concentrations of 10 to 60 percent of monomer yield satisfactory products.

In each case, the polymerization may be interrupted before the infusible product is produced. This may be accomplished by stopping polymerization as the mixture of monomer and polymer begins to grow viscous and before infusible gel formation occurs. In accordance with one illustrative method of interrupting polymerization, the polymer may be separated from the monomer by convenient methods, for example, by the addition of a compound in which the polymers are normally insoluble, such as methyl or ethyl alcohol, petroleum ether, water, ethylene glycol, etc. This process permits the isolation of the fusible polymer in a substantially pure state and is particularly adapted to use when the material is polymerized in solution. Polymerization may also be halted by lowering the temperature of the reaction mixture to a suitable degree, for example, to room temperature or below. In accordance with another effective method of interrupting polymerization, inhibitors such as pyrogallol, hydroquinone, aniline, phenylene diamine, sulphur, thiophenol, organic or inorganic salts or complexes or the reduced forms of metals such as copper, manganese, cobalt, nickel, etc. may be added to the polymer during polymerization or before polymerization has been initiated. When the fusible polymer is produced in solution, it

may also be recovered by slow evaporation or distillation of the solvent. These fusible polymers may be extruded, molded, shaped, or otherwise worked into desirable forms and after final shaping, the products may be completely hardened and rendered infusible by suitable methods herein-after more fully set forth.

In polymerizing the compounds herein contemplated, the time required in order to initiate polymerization and to secure a fusible polymer varies widely in view of slight traces of peroxides or inhibitor which may be present. For this reason, the viscosity of the composition undergoing polymerization is observed and, in general, polymerization is interrupted after the viscosity of the composition undergoing polymerization has approximately doubled. In many cases, subsection of the compound to polymerization conditions for a period of one-half to two hours is sufficient, although some compounds polymerize somewhat more slowly.

Generally, it is preferred to conduct the polymerization in solution in order to secure improved yields. Thus, it is found that the presence of a solvent substantially improves the yield of fusible polymer. Likewise, addition of inhibitor may improve yields although in such a case the rate of polymerization may be comparatively slow.

It is also possible to produce the fusible polymer in accordance with our invention without resorting to the use of solutions of the monomer, although the yield of polymer is, in general, somewhat lower than when a solvent is present. Thus, the monomer may be polymerized directly by use of heat and/or light, preferably in the presence of catalysts, such as air, ozone, oxygen, peroxides, and the like, and interrupting polymerization at the proper time. Since the polymerization may proceed without undue rapidity, with many of these materials, the reaction may be stopped before the infusible gel state is reached without difficulty, either by use of inhibitors or by cooling as hereinbefore mentioned.

The fusible polymers produced by polymerization of undiluted monomer may be molded to any desired shape and subsequently cured to the infusible state. In treating many of these materials, however, it is found that if considerable monomer is retained in the polymer, upon curing considerable difficulty may be encountered in securing complete or substantially complete polymerization of the residual monomer without formation of bubbles, cracks and other defects or without formation of undesirably soft products. Accordingly, we have found that in most cases it is desirable to remove all or a portion of such monomers from the polymer prior to curing the polymer to its infusible state. In accordance with one convenient method, the monomer may be distilled from the polymer under conditions whereby the possibility of further polymerization is minimized, for example, by distillation in a vacuum, preferably at low temperatures and/or in the presence of added inhibitor. Similarly, the monomer may be extracted with a solvent in which the polymer is insoluble such as methyl or ethyl alcohol. Additionally, the polymer and monomer may be separated by dissolving the product in a solvent for both monomer and polymer and adding a non-solvent to precipitate the fusible polymer.

The fusible polymers so produced have many characteristics which are similar to those of usual thermoplastic polymers. They are generally soluble in such organic solvents as acetone, dioxane, benzene, toluene, chloroform, ethyl cellosolve

acetate, triacetin, phenol cellosolve, etc., and soften or flow upon heating under atmospheric pressure. They are precipitated from solutions by use of nonsolvents as white amorphous powder or as plastic semi-liquid resins.

In accordance with our invention, we have found that upon subjection of these polymers to heating at temperatures somewhat above the softening point thereof, for a sufficient period of time, they are converted into infusible, insoluble, transparent, hard and wear-resistant products. This conversion may be assisted by the incorporation of usual polymerization catalysts, such as oxygen, ozone, air, peroxides, such as hydrogen peroxide, or benzoyl peroxide, or other oxygen catalysts, basic or acidic catalysts, light, etc. By use of catalysts, it is found that the conversion of these products to the infusible state may be secured at lower temperatures. In order to secure transparent uniform products the polymerization should be controlled to permit the polymer to flow together, or if desired, to become completely molten prior to converting the polymer to its infusible state. The application of superatmospheric pressure assists the production of satisfactory products.

By operating in accordance with the present invention, we are able to prepare transparent, hard, infusible molded products which have many of the desirable properties of the conventionally known thermoplastic resins as well. By proper regulation of the pressure and temperature, the fusible polymer may be extruded under such conditions that it becomes infusible as it leaves the extrusion dies.

In addition, it is possible to effect a conversion of the exterior of the plastic without completely converting the interior thereof to the infusible, insoluble state. Thus, cast or molded products, made from the fusible polymers herein described may be subjected to local surface heating whereby the surface is converted without complete conversion of the interior. In this manner, it is possible to secure integral products possessing a great flexibility and resiliency, the surfaces of which are extremely hard and insoluble. Similar products may be secured by increasing the catalyst concentration of the fusible polymer adjacent the surface thereof by suitable methods, for example, by application of a coating containing catalysts as described above. Similar products may be secured by incorporation of an inhibitor in the interior of the product or by varying the amount of plasticizer in the interior and exterior portions of the sheet, whereby the interior converts to a flexible gel due to the presence of added plasticizer.

A large number of inert substances may be incorporated with the fusible polymer before subjecting the molding conditions. Suitable for such purposes are: plasticizers, softening agents or fillers, such as dibutyl phthalate, dicyclohexyl phthalate, triacetin, tricresyl phosphate, natural or synthetic resins, pigments, including titanium dioxide, carbon black, chromic oxide, lead chromate, etc., and organic dyestuffs, such as methylene blue, methylorange, etc.

If desired, similar products may be made from suitable copolymers, for example, the esters herein contemplated may be copolymerized with other compatible polymerizable material such as acrylates or alpha-substituted acrylates, for example, methyl, allyl or glycol methacrylate, vinyl acetate, vinyl chloride, styrene; allyl esters such as allyl acetate, maleate, fumarate, phthalate,

succinate, oxalate, tartarate, or the corresponding vinyl, crotyl, methallyl, 2-chlorallyl or other unsaturated alcohol esters to form desirable products in accordance with our invention. Products of widely varying composition containing from 2 to 90 percent of the modifying polymerizable material may be polymerized.

These resins are also suitable for many uses in the field of laminated products. For example, products of great strength, elasticity and adherence may be secured by impregnating fibrous sheets of paper, linen, canvas, etc. with the monomer or polymer herein described, forming a laminated product, and curing the same to an infusible state.

Leather, paper, wood, or other comparatively porous substances may be steeped in a solution of the fusible polymer or a molten body thereof, and one or more layers heated under pressure, generally in the presence of catalyst to convert the absorbed polymer to the infusible, insoluble form. Greatly improved products, particularly in regard to strength, water-proofing and electrical properties are obtained.

The polymers which we have prepared are capable of numerous uses such as in lacquers, or other coating compositions, molded articles, safety glass, etc. Where the composition is used for coating, it may be applied in solution or in solid form, either alone or in combination with natural or synthetic drying oils or resins and the like, the solvent removed and the coated article baked to render the surface infusible. In this manner, it is possible to surface other polymers which are less resistant to the action of solvents or of heat. When a coating of the fusible polymer of the esters herein described is deposited upon polymerized methyl methacrylate or similar polymer, and the solvent removed, a coherent surface thereof is formed. Upon heating the coated article to suitable temperatures, this surface may be made transparent, hard and infusible. Coatings may be applied to metal, glass, wood, synthetic resins, etc. surfaces by extrusion of the heated fusible polymer directly on the suitably-prepared surface. In similar manner, the surface may be heated and the polymer applied in powdered form, whereupon fusion occurs, first to give a smooth homogeneous film which may then be heat-hardened.

The process may also be extended to the production of mixed polymers or copolymers. Thus, the fusible polymer prepared in accordance with our invention may be mixed with other monomers or polymers, such as the monomer or polymer of methyl methacrylate, methyl chloracrylate, vinyl acetate, vinyl chloracetate, vinyl chloride, styrene, etc., and the mixture subjected to conditions of polymerization.

The following examples are illustrative:

Example I

Phosgene was bubbled into a solution containing 1690 grams of allyl lactate per liter of pyridine at a rate of 20 milli-moles per minute while agitating the mixture and cooling to a temperature below about 15 to 20° C. After phosgene in the proportion of about 0.5 mole of phosgene per mole of allyl lactate had been introduced, the mixture was allowed to stand for one hour. Thereafter, the reaction mixture was acidified to the methyl orange endpoint and washed successively with equal volumes of water, dilute hydrochloric acid and dilute aqueous sodium hydroxide, and finally twice with water. The product was

a colorless liquid which boiled at about 154° C. at a pressure of 4 mm. of mercury, and had a density

$$(d_{4}^{20})$$

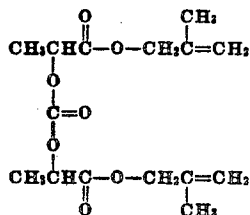
of 1.22 and an index of refraction

$$(n_D^{20})$$

of about 1.4466.

Example II

One mole (98.9 g.) of phosgene was slowly passed into a stirred mixture of 2 moles (288.2 g.) of methallyl lactate and 200 g. of pyridine, while keeping the temperature below 10° C. The resulting slurry was diluted with water and the oily product washed with water, dilute hydrochloric acid and finally with water. Distillation in vacuo gave colorless ester, (B. P. 170-180° C. at 4 mm. pressure) having the probable structural formula



This ester polymerized to a transparent, colorless solid when heated for 12 hrs. at 70° C. with 5% of benzoyl peroxide catalyst.

Example III

A quantity of the carbonate of methallyl lactate prepared as in Example II was mixed with an equal weight of dioxane and 4% benzoyl peroxide on the basis of the weight of the polymer was introduced. The solution was heated, with stirring, at 80 to 85° C. until the viscosity doubled. Thereafter, the mixture was cooled and methanol was added to the point of turbidity. It was then added to 5 volumes of methanol with vigorous stirring. The polymer was separated by decantation, dissolved in acetone, reprecipitated with methanol and again recovered. The polymer was then dried under subatmospheric pressure to constant weight. A white fusible polymer was obtained. A quantity of this polymer was mixed with 5% benzoyl peroxide, placed in a mold and heated to 150° C. under a pressure of 2000 lbs. per sq. in. for 20 minutes. A transparent sheet of infusible, insoluble polymer was obtained.

Example IV

The process of Example III was repeated using the carbonate of allyl lactate in lieu of the methallyl ester and a white fusible polymer was obtained which converted on heating with benzoyl peroxide to a transparent, infusible, insoluble polymer.

Example V

The preparation of vinyl lactate was carried out by passing purified acetylene into a vigorously-stirred solution of anhydrous lactic acid containing mercuric oxide and a complex of boron trifluoride and acetic acid as catalyst. The reaction mixture was neutralized with anhydrous sodium acetate, and the vinyl lactate was recovered by distillation. After further rectification, the pure ester boiled at 50-60° C. under a pressure of 25 mm. of mercury. One mole of vinyl lactate was dissolved in two moles of pyridine, and one-half mole of phosgene was introduced as a slow

stream into the solution, while maintaining vigorous stirring and cooling to below 10° C. After the addition of reactants, the mixture was stirred for several hours and then washed with water, dried, and distilled, the pure carbonate of vinyl lactate was obtained as the fraction boiling at 120-130° C. under a pressure of 4 mm. of mercury.

Although the present invention has been described with reference to the specific details of certain embodiments thereof, it is not intended that such details shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

We claim:

1. A diester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol.
2. A diester of (a) carbonic acid and (b) allyl lactate.
3. A diester of (a) carbonic acid and (b) methallyl lactate.
4. A diester of (a) carbonic acid and (b) vinyl lactate.
5. A polymer of a diester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol.
6. A polymer of a diester of (a) carbonic acid and (b) allyl lactate.
7. A polymer of a diester of (a) carbonic acid and (b) methallyl lactate.
8. A polymer of a diester of (a) carbonic acid and (b) vinyl lactate.
9. A fusible polymer of a diester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol which is capable of being further polymerized prepared by the process of claim 19.
10. A fusible polymer of a diester of (a) carbonic acid and (b) allyl lactate which is capable of being further polymerized to a substantially infusible state prepared by the process of claim 19.
11. A fusible polymer of a diester of (a) carbonic acid and (b) methallyl lactate which is capable of being further polymerized to a substantially infusible state prepared by the process of claim 19.
12. A method of preparing a substantially infusible, insoluble polymer which comprises polymerizing an ester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol, interrupting polymerization after substantial polymerization has occurred, but before the polymer is converted to an infusible gel, separating a substantial portion of residual monomer from the resulting fusible polymer and continuing polymerization of the said polymer for a time sufficient to convert the polymer into a substantially infusible and insoluble state.
13. A method of preparing a substantially infusible, insoluble polymer which comprises polymerizing an ester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol dissolved in a solvent for monomer and polymer, interrupting polymerization after substantial polymerization has occurred, but before the polymer is converted to an infusible gel, separating a substantial portion of residual monomer from the resulting fusible polymer and continuing polymerization of the said polymer for a time sufficient to convert the polymer into a substantially infusible and insoluble state.
14. The process of claim 12 wherein the unsaturated alcohol is allyl alcohol.
15. The process of claim 13 wherein the unsaturated alcohol is allyl alcohol.
16. The process of claim 13 wherein the unsaturated alcohol is methallyl alcohol.

17. The process of claim 12 wherein the unsaturated alcohol is methallyl alcohol.

18. A method which comprises polymerizing a diester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol, interrupting polymerization after substantial polymerization has occurred but before the polymer is converted to a gel, substantially completely separating residual monomer from the resulting fusible polymer, subjecting the polymer to a temperature and pressure sufficient to insure the existence of the polymer in a fused state and polymerizing the

fused polymer to a substantially insoluble infusible state.

19. A method which comprises polymerizing a diester of (a) carbonic acid and (b) a lactic acid ester of an unsaturated alcohol, interrupting polymerization after substantial polymerization has occurred but before the polymer is converted to a gel, and substantially completely separating residual monomer from the resulting fusible polymer.

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